

FABRICATION AND EVALUATION OF CARBON NANOTUBE/ALUMINA COMPOSITES BY PRECURSOR METHOD

K. Shirasu^{1*}, G. Yamamoto¹, Y. Nozaka¹, M. Omori¹, T. Hashida¹

¹Fracture and Reliability Research Institute, Tohoku University, 6-6-11, Aramaki Aoba, Aobaku, Sendai, Japan, 980-8579

*keiichi.shirasu@rift.mech.tohoku.ac.jp

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Abstract

We report the mechanical properties and microstructures of alumina ceramics reinforced with multi-walled carbon nanotubes (MWCNTs) that were surface treated with an acid composed of H₂SO₄ and HNO₃. The acid treatment time was in the range of 0-4 h. Analyses showed that the treated MWCNTs had negatively charged functional groups and nanoscale defects on their surface. In order to evaluate the effects of the acid treatment of the MWCNTs on the mechanical properties and microstructures of the composites, we investigated the dispersibility of MWCNTs and morphology on the fracture surface. We found that the acid treatment was useful to improve the dispersibility of the MWCNTs in the composites, even though their mechanical strength decreased due to the induced nanodefects. The experimental results revealed that the improved dispersibility of MWCNTs overcame their strength reduction and there was an optimal treatment time for enhancing the mechanical properties of the developed MWCNT/alumina composites.

1 Introduction

Recently, researchers have focused on carbon nanotubes (CNTs) which have the outstanding mechanical properties, motivating their use in ceramic composites as a fibrous reinforcing agent. However, the effective utilization of CNTs in composite applications depends strongly on the homogeneous dispersion of individual nanotubes throughout the matrix. Additionally, appropriate interfacial adhesion between the CNTs and the matrix is also required for improving the properties of the composite [1]. It is well known that acid treatments produce negatively charged functional groups on the surface of CNTs [2]. The functional groups make the CNTs easily dispersed in polar solvents, such as water and ethanol [1]. To date, a wide variety of acid treatments have been attempted to improve the dispersion of CNTs [3-5]. However, there is still a lack of quantitative studies to optimize the conditions influencing the dispersion of CNTs in ceramic matrix. In this study, the effects of the duration of acid treatment with H₂SO₄/HNO₃ on the fracture process and the mechanical properties of CNT/alumina composites were investigated for optimization of dispersion of CNTs in the alumina matrix. Furthermore, mechanical strength of the CNTs treated for different times were compared with experimental results of single nanotube tensile tests.

2 Materials and testing methods

Multi-walled carbon nanotubes (MWCNTs) and aluminum hydroxide powders were used as the starting materials [4]. The MWCNT material (acquired from Nano Carbon Technologies) was synthesized by a catalytic chemical vapor deposition method followed by high temperature annealing (Figures 1). The thermal treatment of MWCNTs was carried out at 2600 °C. The diameters and lengths of the pristine MWCNTs from scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements ranged from 33 to 124 nm (average: 70 nm) and 1.1 to 22.5 μm (average: 8.7 μm), respectively. The pristine MWCNTs were refluxed in 3:1 (volume ratio) concentrated H₂SO₄:HNO₃ mixture at 70 °C for 0, 0.5, 1, 2, 3 and 4 h, washed thoroughly with distilled water to be acid-free, and then finally dried in an air oven at 60 °C. The synthesis procedure for the composite is as follows; The pristine or acid-treated MWCNTs were dispersed in ethanol with the aid of ultrasonic agitation. An aluminum hydroxide was added to this solution and ultrasonically agitated. A magnesium hydroxide was added to prevent excessive crystal growth. The resultant suspension was filtered and dried in an oven at 60 °C. The product obtained in the previous step was put into a half-quartz tube and was dehydrated at 600 °C for 15 min in an argon atmosphere. The MWCNT/alumina composites tested in this study were prepared by a spark plasma sintering method in vacuum. A graphite die and punchers with 30 mm diameter were used to form samples. The sintering process was carried out under the conditions: 1500 °C, 10 min and 20 MPa.

The bending strength was measured by the three-point bending method under an ambient condition, in which the size of the test specimens was 2.0 mm (width) × 3.0 mm (thickness) × 24.0 mm (length). The span length and crosshead speed for the strength tests were 20.0 mm and 0.83 μm s⁻¹, respectively. The fracture toughness was measured by the single-edge notched beam (SENB) method under an ambient condition, in which the size of test specimens was 2.0 mm (width) × 3.0 mm (thickness) × 15.0 mm (length). A notch with depth and width of 0.3 mm and 0.1 mm was cut in the center part of the test specimen. A span length of 12.0 mm and crosshead speed of 0.83 μm s⁻¹ were used for the toughness tests. All surfaces of the specimens were finely ground on a diamond wheel, and the edges were chamfered. The nanostructures and microstructures were observed using SEM and TEM. The dispersibility of MWCNTs in the composites (*D*) was estimated by measuring the area of MWCNTs aggregates on the fracture surfaces. *D* was calculated by the following equation:

$$D = \frac{A - A'}{A} \quad (1)$$

where *A* is the sum of the surface area in the recorded SEM images (= 3×10⁻⁸ m²), and *A'* is the sum of the area of MWCNTs aggregates observed in the same SEM images. Eq. (1) indicates that the increment in the *D* corresponds to the improvement of MWCNTs dispersibility in the composites. The changes in zeta potentials were measured in 1.0 mM KCl aqueous solution of varying pH using a zeta potential analyzer. The pH value of the aqueous solution was adjusted with HCl and NaOH. Zeta potential values were calculated using the Smoluchowski equation.

Tensile tests of individual MWCNT was carried out using an in-situ SEM method with a nanomanipulator system [6]. In the tensile tests of individual MWCNT, an AFM cantilever was mounted at the end of a piezoelectric bender on the X–Y linear motion stage, and a W wire was mounted on an opposing Z linear motion stage. MWCNT powder was dispersed in

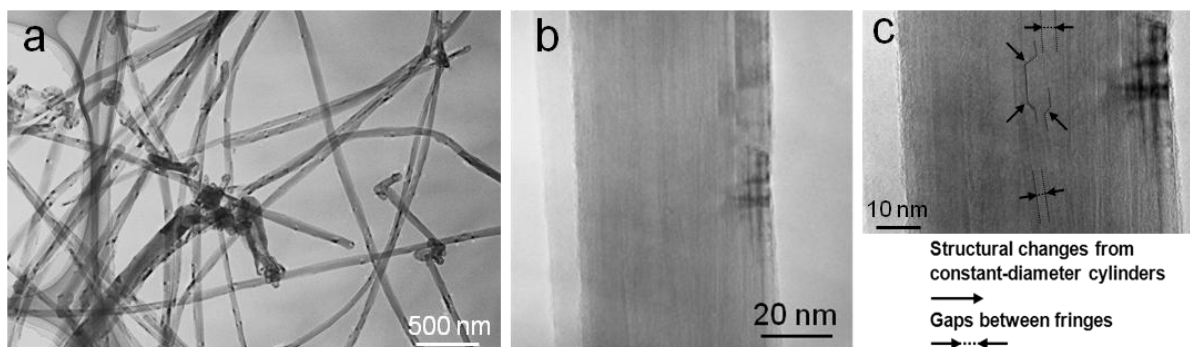


Figure 1. TEM images of the pristine MWCNTs used in this research.

ethanol with the aid of a magnetic stirrer, and then filtered. The resulting MWCNT paper was torn apart by hand, which caused individual MWCNTs to project from the torn edge. Each MWCNT was extracted from the edge, and was then clamped first onto a cantilever tip and then onto an opposing W wire by electron beam induced deposition (EBID) of a carbonaceous material [7]. The cantilevers serve as force-sensing elements and the spring constants of each were obtained in-situ prior to the tensile test using the resonance method developed by Sader et al [8]. The applied force is calculated from the angle of deflection at the cantilever tip, and the nanotube elongation is determined by counting the numbers of pixels in the acquired SEM images. A crosshead speed – i.e., movement rate of the cantilever – of about 100 nm s^{-1} was used for the each test.

3 Results and discussion

To disperse the MWCNTs homogeneously in the matrix, we have used acid treatment of the pristine MWCNTs. The rationale behind the acid treatment is to adsorb negatively charged functional groups at the MWCNT ends and along their length. Figure 1 shows TEM images of the pristine MWCNTs. It can be seen that the pristine MWCNTs have a highly crystalline multi-walled structure with no defects on the wall surface. The detailed structural information of the pristine MWCNTs was retrieved from the enlarged TEM image, as shown in Figure 1c. The pristine MWCNTs are observed to possess unevenly spaced lattice fringes and contain local defects such as kinked layers. It can be seen from Figure 2a that the acid-treated MWCNTs have nanoscale defects on the surface of the MWCNT. The defects in these acid-treated MWCNTs had a channel-like structure, as if a ring of material was cut away from the MWCNT around the circumference, and the defects density, namely the number of defects per unit of MWCNT surface area increased with increasing the acid treatment time. The depth of nanodefects are increased with the increasing acid treatment time up to 2 h and levels off for the longer treatment times (Figure 2c). In contrast, TEM observations revealed that peel-off of a few layers in the MWCNT structure was observed for the MWCNTs acid-treated for 3 and 4 h (Figure 2b). Thus, no significant difference in the depth of nanodefects may be due to the peel-off of in the MWCNT structure by the excessive acid treatment when the acid treatment time is longer than 2 h.

Figure 3a shows the zeta potential values of the pristine MWCNTs and acid-treated MWCNTs at different pH values. The isoelectric point (pH_{iep}) for the pristine MWCNTs is located at about 3.0, whereas the acid treatment makes the surface more negatively charged at tested pH values, and their zeta potential values decreased gradually with increasing pH regardless of the acid treatment time. The pH value was about 10 for the mixing process of aluminum hydroxide and MWCNTs. Therefore, the zeta potential values of the pristine MWCNTs and acid-treated MWCNTs at $\text{pH}=10$ are measured (Figure 3b). With increasing the acid treatment time from 0 to 2 h, the zeta potential values of the MWCNTs powders were

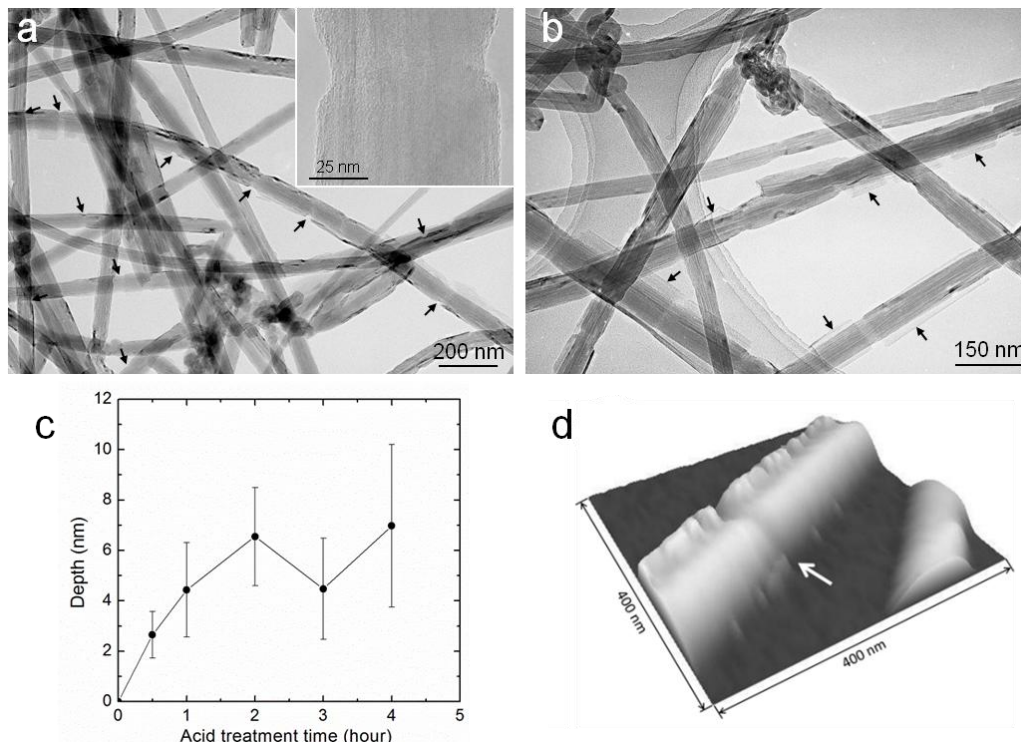


Figure 2. (a) TEM and (d) AFM images of the MWCNTs acid-treated for 2 h. The inset in the (a) shows the high-magnification image of the acid-treated MWCNT. (b) TEM image of the MWCNTs acid-treated for 3 h. (c) Relationship between acid treatment time and depth of the nanoscale defects.

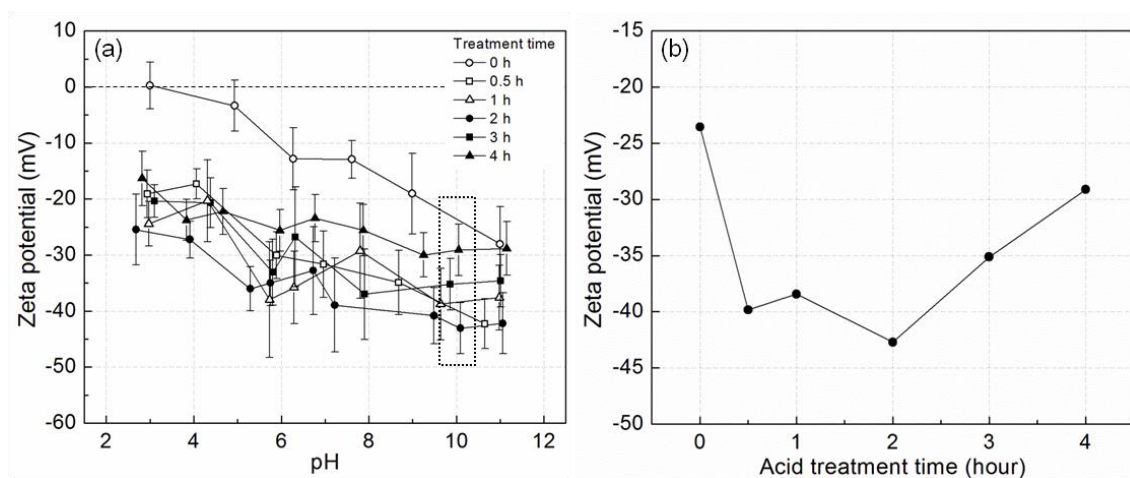


Figure 3. Zeta potential values of the pristine MWCNTs and acid-treated MWCNTs (a) at different pH and (b) at pH=10.

markedly decreased, and then increased from 2 to 4 h. The increase in the zeta potential values measured for the longer acid treatments may be due to the peel-off of a few layers in the MWCNT structure by the excessive acid treatment of the MWCNTs. The change in the zeta potential is due to mainly the further introduction of functional groups on the surface of the MWCNT after the acid treatment. These functional groups may make them easily dispersed in polar solvents, such as water and ethanol. Furthermore, it can be expected that the larger electrical repulsive force between the acid-treated MWCNTs will facilitate their dispersion and prevent them from tangling and agglomeration. Therefore, the reduction in the zeta potential values measured for the excessive acid treatments may be attributable to the decrease of the amount of the functional groups by peel-off of a few layers in the MWCNT

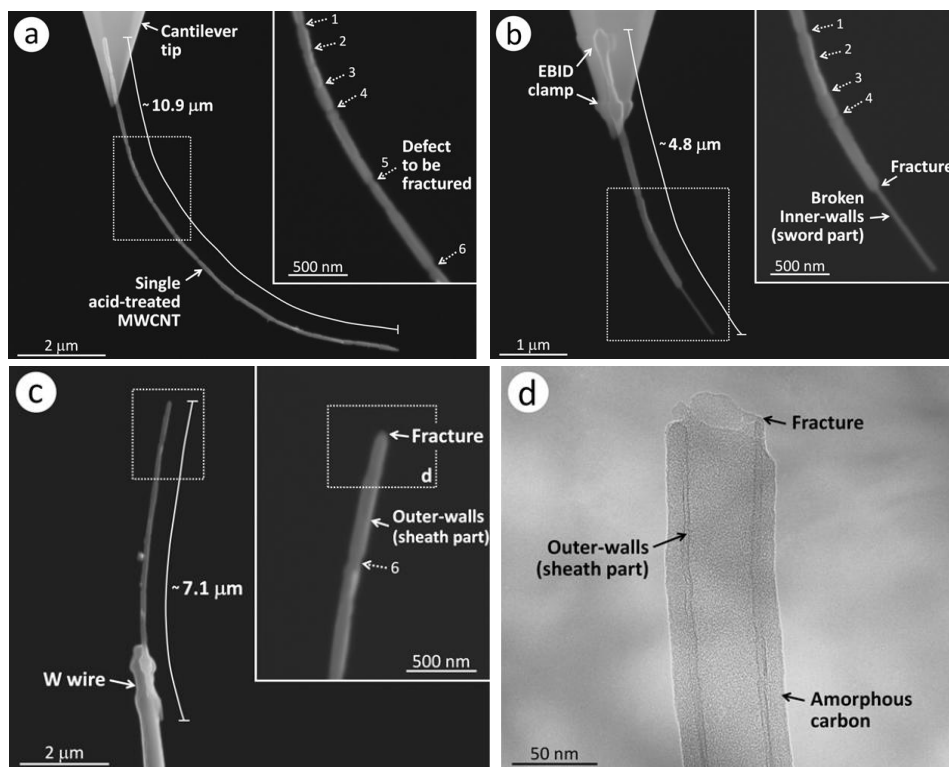


Figure 4. (a, b, c) Fracture of the acid-treated MWCNT captured in a series of SEM images. The dashed white arrows in the insets indicate the position of the nanoscale defects. (d) TEM image shows a "sword-in-sheath"-type failure.

structure. In order to study the dispersion stability of the MWCNTs, the samples were suspended in 50 ml ethanol and their suspensions were treated by an ultrasonic agitator for 15 min and then allowed to stand for about 15 min. We can see that large settleable aggregates had formed for the pristine MWCNTs, while for acid-treated MWCNTs, apparently uniform MWCNT/ethanol solution was attained without visible aggregates.

In order to investigate the effects of the acid treatment on the mechanical properties of the individual MWCNT, the tensile tests of single MWCNT were carried out. A series of SEM images of an individual acid-treated MWCNT acquired before and after fracture are shown in Figures 4. A $10.9 \pm 0.1 \mu\text{m}$ -long section of this MWCNT was attached and then loaded and it fractured in the middle. The resulting fragment attached on the cantilever tip had a length of at least $4.8 \pm 0.1 \mu\text{m}$, whereas the other fragment on the W wire had a length of at least $7.1 \pm 0.1 \mu\text{m}$. Thus, the sum of the fragment length far exceeded the original section length. This apparent discrepancy can be explained as due to a "sword-in-sheath"-type failure, similar to that observed in the failure mode of arc-discharge-grown MWCNTs and certain types of carbon fibers. Similar "sword-in-sheath" failure was observed in all MWCNTs tested. Figure 5 shows the dependence of breaking force of the MWCNT on acid treatment time. The breaking force decreased as the acid treatment time increases to 2 h. While, no clear difference in the breaking force is observed between the MWCNTs with treatment time of 2 and 4 h. The measured breaking forces of the acid-treated MWCNTs with treatment time of 0 (i.e. pristine), 2 and 4 h were 6.1 ± 2.0 , 4.5 ± 1.5 and $4.8 \pm 1.2 \mu\text{N}$, respectively. As described above, the depth of nanodefects on the surface of the MWCNT are increased as the acid treatment time increases up to 2 h and levels off for the longer treatment times. Therefore, we infer that the reduction of the breaking force may be due to the effect of the depth of nanodefects that were introduced on the surface of the MWCNT by the acid treatment.

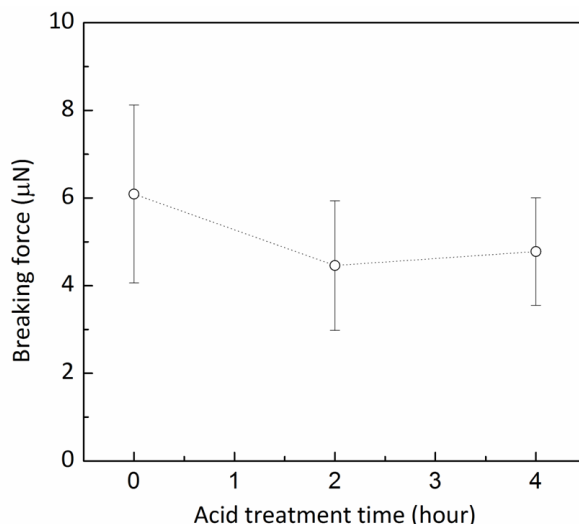


Figure 5. Breaking forces of the MWCNT as a function of acid treatment time.

Figures 6 show the microstructure of the fracture surface of the 1.9 vol.% MWCNT/alumina composite. From the fracture surface, the following features can be noted. First, numerous individual MWCNTs protrude from the fracture surface, and the pullout of the MWCNTs can be clearly observed. The MWCNTs are located in the intergranular phase and their lengths are in the range of 0-10 μm . Second, some MWCNTs showed that the diameter of pullout MWCNT drastically slenderized toward their tip. TEM observations on the fracture surface demonstrated that a diameter change in the MWCNT structure was evidently observed for a certain percentage of the MWCNTs regardless of the acid treatment time, and this morphology is quite similar to a "sword-in-sheath"-type failure as observed in the failure mode of MWCNTs under tensile loading (Figure 6c). Note that MWCNT failure was also observed in the fracture surfaces of the alumina composites made with the pristine MWCNTs [9]. Since no apparent variation in the diameter of the MWCNTs has been observed along the axis in the as-received MWCNTs, these results imply that some MWCNTs underwent failure prior to pullout from the matrix. Third, the fracture surface of the composites revealed good

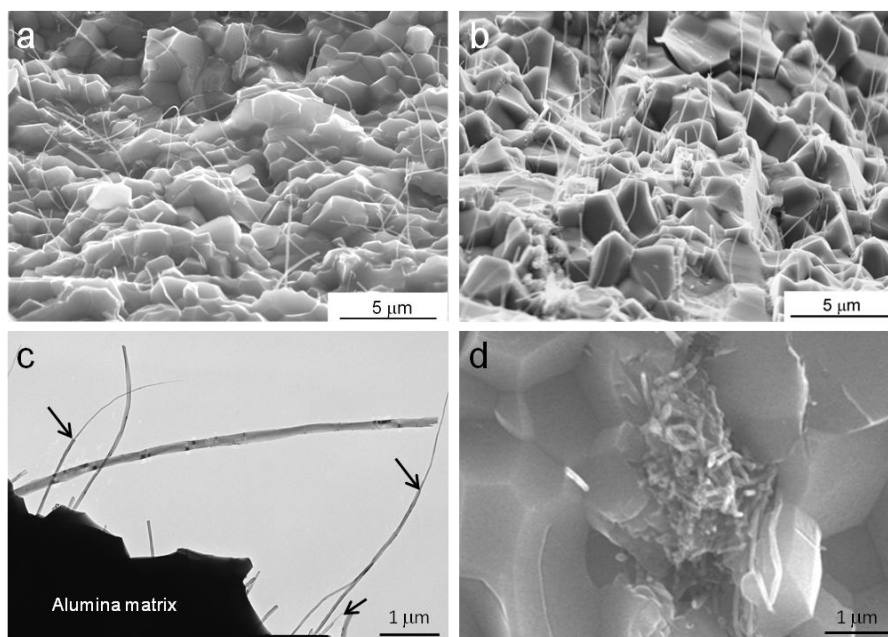


Figure 6. Fracture surface of the alumina composites made with (a, d) pristine MWCNTs and (b) MWCNTs acid-treated for 2 h. (c) TEM image of the fracture surface of the acid-treated MWCNT/alumina composite.

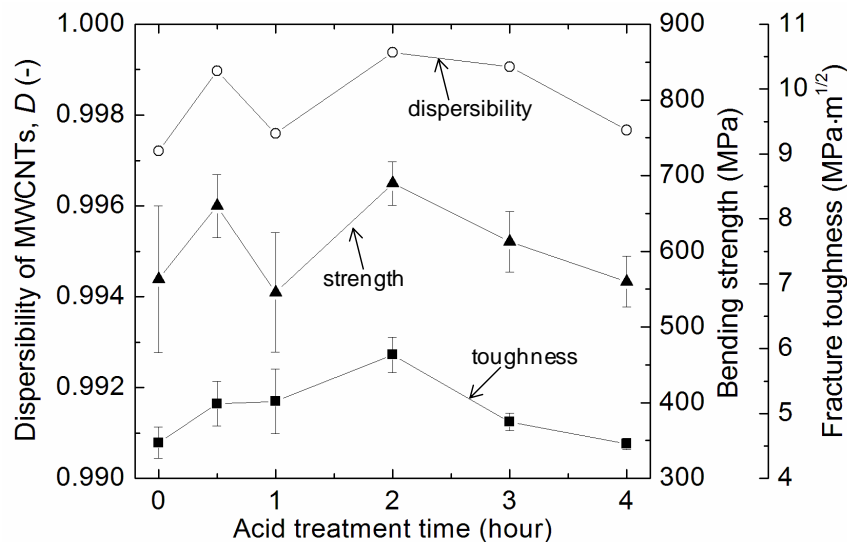


Figure 7. Relationship between dispersibility of MWCNTs and mechanical properties of the composites.

dispersion of MWCNTs within the matrix. In the case of the smaller amount of the acid-treated MWCNTs, no phase segregation was observed. The composites made with the pristine MWCNTs, however, revealed an inhomogeneous structure, as shown in Figure 6d. In order to evaluate the effects of the MWCNTs aggregates on the mechanical properties of the composites, the dispersibility of MWCNTs in the composites (D) was estimated by measuring the area of MWCNTs aggregates on the fracture surfaces. Figure 7 shows the relationship between dispersibility of the MWCNTs and mechanical properties of the composites with 0.9 vol.% MWCNTs. We found that the bending strength and fracture toughness of the composites were correlated highly with the dispersibility of the MWCNTs in the matrix. The dispersibility of MWCNTs and mechanical properties of the composites were simultaneously increased up to 2 h, and then they were decreased gradually with increasing acid treatment time. The improvement in the mechanical properties due to the acid treatments up to 2 h may be attributable to the better dispersion of the MWCNTs in the matrix. On the other hand, the excessive acid treatment of the MWCNTs resulted in degradation of the dispersibility of MWCNTs and mechanical properties of the composites due to the decrease in the number of the negatively charged functional groups by the peel-off of a few layers in the MWCNT structure. These results imply that there is an optimal acid treatment time for enhancing the mechanical properties of the composites.

It is well recognized the fracture properties of fiber-reinforced composites are dominated by the fiber bridging force resulting from debonding and sliding resistance, which dictates the major contribution to the strength and toughness [10]. According to the single nanotube tensile tests, 27 and 21% reductions in the breaking force were observed for the MWCNT with treatment time of 2 and 4 h, respectively. Furthermore, as mentioned above, TEM observations on the fracture surface demonstrated that MWCNT failure has been evidently observed for all kinds of the MWCNTs in the present research. Based on the correlation indicated in Figure 7, the improved dispersibility of the MWCNTs acid-treated for 1-2 h appears to be an overriding factor rather than the strength reduction of single MWCNT due to the induced nanodefects by the acid treatment. More detailed discussion calls for further investigation regarding possibly altered interfacial properties by the acid treatment, as well as effects of the use of stronger MWCNTs on the mechanical properties of MWCNT composites.

4 Conclusions

It has been demonstrated that there is an optimal acid treatment time for improving the mechanical properties of the MWCNT/alumina composites. The dispersibility of the MWCNTs and mechanical properties of the composites were increased as the acid treatment time increased up to 2 h, and then they were decreased gradually with the increasing acid treatment time. The excessive acid treatment of the MWCNTs resulted in degradation of the dispersibility of MWCNTs and the mechanical properties of the composites due to the decrease in the number of the negatively charged functional groups by the peel-off of a few layers in the MWCNT structure. According to the tensile tests of individual MWCNT, the breaking force of the MWCNT decreased as the acid treatment time increased up to 2 h, and leveled off for the longer treatment times. In contrast, MWCNT failure has been evidently observed regardless of the acid treatment time through TEM observations. These results revealed that the improved dispersibility of MWCNTs overcame their strength reduction, and the high structural homogeneity is much more effective for enhancing the mechanical properties of the developed MWCNT/alumina composites.

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